EYRING'S EQUATION OF RELAXATION TIME AND DIELECTRIC ABSORPTION OF 3.14 cm MICRO-WAVES IN POLAR LIQUIDS—PART III. SUBSTITUTED TOLUENES AND α-BROMONAPHTHALENE

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ABSTRACT. The results of measurement on the times of relaxation of *o* , *m* and *p*-chlorotoluenes, *p*- bromotoluene, 3, 4-dichlorotoluene and α-bromonaphthalene in the liquid state at different temperatures and also the experimental values of the activation energies (ΔH_τ) for dipole orientation are reported. An attempt has been made to correlate the experimental activation energies with the total energy due to intermolecular forces operating in the polar liquids. Following Eyring's theory of rate process, an expression for the 'frequency factor' has been deduced. The theoretical values have been compared with the experimental values for the frequency factor in the case of a number of polar organic compounds.

INTRODUCTION

Both Debye's theory and Eyring's theory of rate process have been applied to the elucidation of the mechanism of dipole rotation accompanying the phenomenon of dilectric relaxation in polar liquids subjected to rapidly alternating electric fields. The Debye's theory and some of its modifications (Perrin, 1939; Writz, 1954; Hill, 1954) have been used, chiefly, to obtain information about the molecular unit taking part in the dipole rotation and the internal viscous forces hindering such rotations. Eyring's theory on the other hand have yielded experimental values of heats of activation and entropy of activation required for the orientation of dipoles (Whiffen and Thompson, 1946; Fong and Smyth, 1963; Bhattacharyya *et al.*, 1966). While the limitations of the Debye's theory in determining the dimensions of the rotating dipole are well- known, the relation of the activation energy and the entropy of activation with the molecular parameters of the dipole is not obtained from the rate equation itself. Very little attempt has been made to correlate the experimental activation energy with the energy of the intermolecular forces obtaining in the polar liquids. Moreover, no method exists for obtaining an estimate of the entropy change in the relaxation process, which, incidentally is contained in the so called "frequency factor" obtained experimentally, from the molecular properties of the polar liquids.

Bhanumathi (1963) made attempt to identify the activation energies for dipole orientation in some organic polar liquids with the energy of interaction due to dipole dipole (Keesom) and dipole-induced dipole (Debye) forces between the molecules of the liquids. She obtained a fair amount of agreement between the experimental and the calculated energy values. Recently, Sinha *et al*, (1966) have shown that in the case of very dilute solutions of polar compounds in non-polar solvents, the values of the activation energy calculated from a consideration of the interaction energy due to London's dispersion forces and the Debye forces agree fairly well with the activation energies obtained experimentally.

In the present paper an attempt has been made to calculate (i) the values of the activation energy by considering the total contributions from London, Keesom and Debye forces existing in the polar liquids and (ii) the value of the "frequency factor" from the parameters of the polar molecules. In order to find out how far the calculated values agree with the experimental values, the data on the activation energies and frequency factors obtained experimentally for a number of polar organic liquids in the present investigation and in earlier investigations (Bhattacharyya *et al.*, 1964, 1966) have been used.

EXPERIMENTAL

Chemically pure samples of *o*-, *m*- and *p*-chlorotoluenes, *p*-bromotoluene, 3, 4-dichlorotoluene and α-bromonaphthalene obtained from reputed chemical firms were first fractionated and the proper fractions were repeatedly distilled under reduced pressure. The samples were properly dried before being used in the investigations. The experimental arrangement for determining the dielectric loss at 3-cm at different temperatures and the method of obtaining the time of relaxation (τ) were the same as described in the previous paper (Bhattacharyya *et al.*, 1966). The viscosities (η) of all the liquids were determined experimentally.

RESULTS AND DISCUSSION

The values of ϵ', ϵ'', $\tan\delta$ and τ along with the macroscopic viscosities (η) of all the compounds at different temperatures (T) are given in Tables I-VI. The values of the heat of activation for dielectric relaxation (ΔH_τ) and viscous flow ($\Delta H\eta$) have been obtained respectively from the graphs of log ($\tau.T$) against $1/T$ and log η vs $1/T$ as usual. These values and their ratios (γ) are given at the foot of the tables. The tables also contain the values of $\tau.T/\eta^\gamma$ and the average value of the frequency factor A obtained from the rate equation $\tau = AT^{-1} \exp(\Delta H_\tau/RT)$ for all the compounds. It is seen from the Tables that in each case $\tau.T/\eta^\gamma$ remains almost constant with temperatures. Similar relation was also observed with other compounds reported previously (Bhattacharyya *et al*, 1966). In the following sections attempts have been made to calculate the activation energy and the frequency factor.

TABLE I

o-Chlorotoluene

Wave length (λ) = 3.14 cm

Temp. °K	ε'	ε''	tan δ	$\tau \times 10^{12}$ Sec	η m.p.	$\frac{\tau.T}{\eta^{\gamma}} \times 10^{7}$
288	3.80	1.20	0.317	13.6	11.2	15.31
298	3.81	1.13	0.297	12.7	9.9	15.52
313	3.99	1.13	0.283	11.3	7.8	15.92
328	4.08	1 04	0.255	9.7	6.3	15.81
343	4.02	0.88	0.220	8.7	5.4	15.44
358	4.05	0.84	0.208	8.1	4.5	16.17

ΔH_{τ} = 1.07 K.Cal/mole $\quad \gamma = 0.39$

ΔH_{η} = 2.75 K.Cal/mole $\quad A = 62.1 \times 10^{-11}$

TABLE II

m-Chlorotoluene

Wave length (λ) = 3.14 cm

Temp. °K	ε'	ε''	tan δ	$\tau \times 10^{12}$ Sec	η m.p.	$\frac{\tau.T}{\eta^{\gamma}} \times 10^{7}$
278	3.76	1 95	0.519	22.5	11.1	25.72
298	3.74	1.64	0.438	19.2	8.5	26.47
313	3.79	1 49	0.393	16 8	6.8	26.37
328	3.82	1.36	0.356	15.0	5.6	26.46
343	3.76	1.17	0.312	13.5	4.8	26.32
358	3.76	1.13	0.301	13.0	4.4	27.30

ΔH_{τ} = 0.89 K.Cal/mole $\quad \gamma = 0.36$

ΔH_{η} = 2.50 K.Cal/mole $\quad A = 126.5 \times 10^{-11}$

TABLE III

p-Chlorotoluene

Wave length (λ) = 3.14 cm

Temp. °K	ε'	ε''	tan δ	$\tau \times 10^{12}$ Sec	η m.p.	$\frac{\tau.T}{\eta^{\gamma}} \times 10^{7}$
298	3.79	2.18	0.575	24.6	8.9	37.21
313	3.83	1.93	0.504	21.2	7.0	36.29
328	3.86	1.83	0.474	19.7	5.7	37.68
343	3.84	1.71	0.445	18.6	4.9	38.98
358	3.89	1.56	0.401	16.4	4.3	37.36

ΔH_{τ} = 0.78 K.Cal/mole $\quad \gamma = 0.31$

ΔH_{η} = 2.56 K.Cal/mole $\quad A = 204.6 \times 10^{-11}$

TABLE IV

p-bromotoluene

Wave length (λ) = 3.14 cm

Temp °K	ε'	ε''	tan δ	$\tau \times 10^{12}$ Sec	η m.p.	$\frac{\tau.T}{\eta^{\gamma}} \times 10^{7}$
313	3.34	1.54	0.461	27.3	9.5	38.86
328	3.45	1.53	0.444	24.3	7.7	39.02
343	3.47	1.44	0.415	22.4	6.6	39.98
358	3.59	1.42	0.396	19.9	5.8	38.50

$\Delta H\tau$ = 0.89 K.Cal/mole $\quad \gamma$ = 0.35

$\Delta H\eta$ = 2.51 K.Cal/mole $\quad A = 209.9 \times 10^{-11}$

TABLE V

3, 4-dichlorotoluene

Wave length (λ) = 3.14 cm

Temp °K	ε'	ε''	tan δ	$\tau \times 10^{12}$ Sec	η m.p.	$\frac{\tau.T}{\eta^{\gamma}} \times 10^{7}$
303	3.30	2.16	0.655	38.9	13.7	18.36
318	3.33	1.82	0.547	31.8	10.3	19.30
333	3.58	1.76	0.492	24.2	8.5	17.63
348	3.68	1.66	0.451	21.2	6.7	19.11
363	3.76	1.57	0.418	18.9	6.2	18.80

$\Delta H\tau$ = 2.20 K.Cal/mole $\quad \gamma = 0.71$

$\Delta H\eta$ = 3.10 K.Cal/mole $\quad A = 29.6 \times 10^{-11}$

TABLE VI

α-bromonaphthalene

Wave length (λ) = 3.14 cm

Temp. °K	ε'	ε''	tan δ	$\tau \times 10^{12}$ Sec	η m.p.	$\frac{\tau.T}{\eta^{\gamma}} \times 10^{7}$
303	2.93	0.96	0.328	88.9	40.5	43.89
313	2.99	1.03	0.344	71.3	31.6	37.93
328	3.05	1.07	0.351	59.4	22.4	42.29
343	3.12	1.11	0.356	50.0	16.6	43.30
358	3.19	1.21	0.379	45.8	12.6	47.40

$\Delta H\tau$ = 2.30 K.Cal/mole $\quad \gamma$ = 0.49

$\Delta H\eta$ = 4.72 K.Cal/mole $\quad A = 56.6 \times 10^{-11}$

a) *Calculation of interaction energy*

In order to obtain an estimate of the energy due to various intermolecular forces existing in polar liquids, special type of interaction e.g. hydrogen bonding etc. has been left out of consideration. The three main types of intermolecular forces considered are (i) London dispersion forces, (ii) Dipole-Dipole (Keesom) forces and (iii) Dipole induced dipole (Debye) forces (Ketelaar, 1953). So that the

total interaction energy is the sum of the energies due to each of the forces. The energy of interaction per molecule for the three types of forces are given by :

(i) London energy $E_L = \frac{3}{} \; I\alpha^2$

ii) Keesom energy $E_K = -\frac{2}{3} \; \frac{\mu^4}{kTr_0^6}$

iii) Debye energy $E_D = -2 \; \alpha\mu^2/r_0^6$ ... (1)

where I is the ionisation potential of the molecule, α and μ respectively are the polarisability and the dipole moment of the molecule, r_0 is the average distance of separation between the dipolar molecules and k is the Boltzmann constant. The total interaction energy per molecule, $-U_m = E_L+E_K+E_D = E_L(1+f_1+f_2)$

where $f_1 \; \frac{E_K}{E_L} - \frac{8}{9} \; \frac{\mu^4}{I\alpha^2kT}$ and $f_2 = \frac{E_D}{E_L} \; \frac{8}{3} \; \frac{\mu^2}{I.\alpha}$ (2)

If I is expressed in e.v. μ in Debye unit, r_0 in Å and α in units of 10^{-25} cc., then for a temperature $T = 333.3°K$

$$f_1 = 1208.1\mu^4{}_D/I_e\alpha_p{}^2, \qquad f_2 = 16.67\mu^2{}_D/I_e\alpha_p$$

and $$E_L = -\frac{1.2I_e\alpha^2{}_p}{r_A{}^6} \times 10^{-14} \text{ ergs/molecule} \quad (3)$$

Further, if the average distance r_A is calculated from the equation $r_A = \beta R_A$ where β is a constant and $R_A = (1.66V_M)^{1/3}$Å, V_M being the molar volume in cc., E_L may be written as

$$N.E = -\frac{.0627I_e}{\beta^6}(\alpha_p/V_M)^2 \; K.\text{cal/mole} \quad (4)$$

Since the activation energy is $-(-U) = U = NU_m$, where, N = Avogadro Number

$$U = \frac{.0627I_e}{\beta^6}\left(\frac{\alpha_p}{V_M}\right)^2 (1+f_1+f_2) \; K.\text{cal/mole} \quad \ldots (5)$$

If this value of U is identified with the heat of activation ΔH_r it is possible to calculate the value of β and to find out how far this value remains constant for the

different compounds. The value of β may also be estimated from the ratio of the free volume to the molar volume of the compound given by the relation $\beta_e = \left(\frac{V_M - v_0}{V_M}\right)^{1/3}$ where v_0 is the total volume of all the molecules in a gram molecule of the compound. This value of β_e is expected to be equal to that of β for molecules having very small dipole moments where E_K and E_D are negligible.

In order to find out how far the above considerations are consistent with the experimental results, all the necessary data have been collected in Table VII. The ΔH_τ-values for compounds other than those obtained in the present investigation have been taken from the previously published data (Bhattacharyya *et al.*, 1964, 1966). The dipole moment (μ_D) and the molecular polarisability values (α_p) whenever available, have been taken from published literatures. In other cases α_p-values have been calculated from the molar volume and refractive index data. The values of the Van der Waal's constant $b = 4v_0$ have been calculated from the data on critical constants given in "physical properties of chemical compounds (15)". The data on ionisation potential have been taken from the published works (Kandel, 1955; Watanabe, 1957; Vilesov and Terenin, 1957; Streiswiesser, 1960) and in the cases of *m*-dichlorobenzene, α-chloro- and α-bromo naphthalenes, the ionisation potential have been taken to be almost equal to that of the parent compounds.

It is seen from Table VII that except for molecules whose dipole moment $\sim 2D$ the contributions due to Keesom and Debye forces are small. The value of β varies between 0.8—1.0. While the values of β_e estimated from $\left(\frac{V_M - v_0}{V_M}\right)^{1/3}$ agrees roughly with the calculated β-values in the case of the alkyl benzenes, the disagreement between the two values increases as the dipole moment of the molecule increases. Considering the highly approximate nature of the calculations, the agreement is fairly satisfactory.

b) *Calculation of the 'frequency factor'*

The experimental value of the 'frequency factor' A is obtained from the time of relaxation τ at a temperature $T°K$ for a particular compound from the relation

$$\tau = AT^{-1} \exp(\Delta H_\tau / RT) \qquad \ldots (6)$$

The quantity A which has the dimension of sec. deg. is not equal to $h/k = 4.8 \times 10^{-11}$ as is sometimes assumed, but is given from the Eyring's rate equation by the expression $A = h/k \exp(-\Delta S/R)$ where ΔS is the entropy of activation for the process of dipole orientation. Since Eyring has given no theoretical expression for determining the quantity ΔS we proceed to obtain the value of A from Eyring's fundamental rate equation (Glasstone *et al.*, 1941) given by

$$K_1 = \frac{kT}{h} \frac{F^{\ddagger}}{F} \exp(-U/RT) \qquad \ldots (7)$$

TABLE VII

$$U = \Delta H_\tau = \frac{.0627 I_e}{\beta^6} \cdot \left(\frac{\alpha_p}{V_M}\right)^2 (1+f_1+f_2)$$

$$\beta_e = \left(\frac{V_M - v_0}{V_M}\right)^{1/3}, \quad b = 4v_0$$

Compound μ_D	Polarisability $\alpha_p \times 10^{25}$cc (V_M)	Ionisation potential I_e ev (bcc/mole)	$f_1 = \frac{Ek}{E_L}$ $\times 10^2$	$f_2 = \frac{E_D}{E_L}$ $\times 10^2$	ΔH_τ K.Cal/mole	β	β_e
Toluene .30	122.6 (111)	9.03 (146.3)	.007	.136	1.60	.868	.878
o-Xylene .51	141.0 (125)	8.77 (175.5)	.047	.351	1.53	.877	.848
m-Xylene .30	141.8 (128)	8.79 (177.2)	.006	.120	1.44	.822	.868
Ethyl benzene .36	141.0 (128)	8.70 (166.7	.011	.168	2.20	.833	.877
Isopropyl benzene .40	156.0 (145)	8.70 (202.5)	.013	.184	2.90	.790	.867
Chloro benzene 1.56	122.5 (102)	8.80 (145.3)	5.41	3 76	1.19	.951	.864
Bromo benzene 1.50	136.0 (106)	8.98 (153.9)	3.68	3.07	1.49	.933	.860
m-dichloro benzene 1.48	142.3 (115)	9.00 (183.3)	3.18	2.85	1.02	.982	.848
o-Chloro toluene 1.43	141.6 (117)	8.88 (178.1)	2.84	2.71	1.07	.965	.853
m-Chlorotoluene 1.94	142.4 (118)	8.88	6.59	4.12	0.89	.985	—
p-Chloro toluene 1.94	142.4 (118)	8.82	9.57	5.00	0.78	1.005	—
p-Bromo toluene 1.96	155.0 (123)	8.69 (186.4)	8.54	4.76	0.89	.995	.853
α-Chloro naphthalene 1.50	193.0 (135)	8.00	2.05	2.43	2.71	.851	—
α-bromo naphthalene 1.50	197.0 (140)	8.00	1.97	2.38	2.30	.870	—

where $K_1 = 1/\tau$, U is the activation energy per mole, F is the total partition function per unit volume of the normal molecule and F^* is that of the activated molecule, excluding the contribution of the degree of rotational freedom along the reaction co-ordinate i.e. the angle of rotation of the dipole. We may assume that the electronic and vibrational contributions to the partition functions for the normal and the activated molecules to be the same. As regards the rotational contribution it may be observed that in the normal molecule, the dipole moment makes rotational oscillation of small amplitude and small frequency about its instantaneous position of orientational equilibrium, which in the activated molecule is converted into one of free rotation, the contribution due to which has already been included in equation (7). It is also assumed that the rotation about the two other axes are non-existent both in the normal and in the activated molecule. In the case of the normal molecule the rotational oscillational contribution to the partition function is $\approx kT/h\nu_0$ where ν_0 is estimated from the relation $2\pi\nu_0 = (\Omega/J)^{\frac{1}{2}}$ where J is the moment of inertia of the molecules about an axis perpendicular to the dipole moment. If the dipole moment is along the a-axis of the ellipsoidal molecule then J is intermediate between J_B and J_C. Ω is the restoring potential and is of the order of $3(E_K+E_D)$ in the polar liquids.

The translational contribution per molecule to the partition function for the activated molecule which may be supposed to be moving freely in a volume v = (vol. of liquid per molecule) is $(2\pi mkT/h^2)^{3/2}.v$ (Frenkel, 1946). In the case of the normal molecule, however, the translational degrees of freedom are replaced in the liquid state by translational oscillations in the three mutually perpendicular directions about the mean equilibrium position of the molecule and the contribution to the partition function is $(kT/h\nu_l)^3$(Frenkel, 1946) where ν_l is given by the equation $2\pi\nu_l = (f/m)^{\frac{1}{2}}$ and $f = (\partial^2 U_m/\partial r^2)_{eqlb}$. Since U_m is of the form B/r^6, f is obtained as $f = 42U_m/r_0^2$, U_m is the potential energy per molecule and m is the mass of the molecule.

Substituting these values in Eqn (7) the following expression for τ is obtained.

$$\tau = \frac{h}{kT}\left[\left(\frac{2\pi RT}{U}\right)^{3/2} \frac{kT}{(42)^{3/2}v} \frac{v}{h\nu_0}\right] e^{U/KT} \qquad (8)$$

If $r_0^3 \approx v$ and ν_0 is replaced by $\bar{\nu}_0 = \frac{\nu_0}{c}$, Eqn. (8) takes the form

$$\tau = \frac{h}{kT}\left\{\left(\frac{2\pi RT}{U}\right)^{3/2} \frac{kT}{(42)^{3/2}hc\bar{\nu}_0}\right\} e^{U/RT} \qquad \ldots \quad (8a)$$

Comparing Eqn. (8a) with Eqn. (6) the frequency factor A is given by

$$A = \frac{h}{k}\left\{\left(\frac{2\pi RT}{U}\right)^{3/2} \cdot \frac{kT}{(42)^{3/2}hc\bar{\nu}_0}\right\} \qquad \ldots \quad (9)$$

For $T = 333.3°K$ substituting the values of R, h, k and c, A is finally given as

$$A = \frac{7.29}{\bar{\nu}_0 U^{3/2}} \cdot \frac{h}{k} \qquad \ldots \quad (9a)$$

TABLE VIII

$$A = \frac{7.29}{U^{3/2}\bar{\nu}_0} \cdot \frac{h}{k}$$

Compound	$A \times 10^{11}$ (experimental)	A (calculated) $\times 10^{11}$	
		$\bar{\nu}_0 = 1$ cm^{-1}	$\nu_0' = 0.5$ cm^{-1}
Toluene	14.3	18.1	36.3
o-Xylene	22.1	18.0	35.9
m-Xylene	31.3	22.3	44.6
Ethyl benzene	8.1	12.2	24.4
Isopropyl benzene	2.8	7.4	14.8
Chlorobenzene	40.2	27.0	53.9
Bromobenzene	36.4	19.2	38.5
m-dichloro benzene	71.6	34.0	67.9
1, 2, 4-Trichloro benzene	126.8	29.9	59.8
o-Chlorotoluene	62.1	31.6	63.2
m-Chlorotoluene	126.5	41.7	83.3
p-Chlorotoluene	204.6	50 8	101.6
p-bromotoluene	209.9	68.9	137.8
3, 4-dichloro toluene	29.6	10.7	21.4
α-Chloro naphthalene	15.5	6.9	13.8
α-bromo naphthalene	56.6	10.0	19.9

Eqn. (9a) shows that A does not have the value h/k but varies from molecule to molecule depending on U and $\bar{\nu}_0$. The value of $\bar{\nu}_0$ estimated in the case of toluene from the equation $2\pi c\bar{\nu}_0 = (\Omega/J)^{\frac{1}{2}}$ is of the order of 1 cm^{-1}. With halo substituted benzenes, toluenes and naphthalenes the values of $\bar{\nu}_0$ are expected to be smaller than 1 cm^{-1} because of the substantial increase in the values of the moment of inertia (J) of the molecules. The value of the frequency factor A calculated for two values of $\bar{\nu}_0$ are given in Table VIII along with the experimental values of A. It is seen from the table that the experimental value of A in the case of the alkyl benzenes agrees fairly with the calculated A-value if $\bar{\nu}_0 = 1$ cm^{-1}, while in the case of chlorobenzene bromobenzene, *m*-dichlorobenzene, *o*-chlorotoluene, 3, 4-dichlorotoluene and α-chloronaphthalene fair agreement is obtained if $\bar{\nu}_0$ is taken to be

0.5 cm^{-1}. In the case of *m*-chloro toluene, *p*-chloro-and *p*-bromotoluene and α-bromonaththalene the assumed value of $\bar{\nu}_0$ is to be further reduced in order that the calculated A-values agree fairly with experimental values of A.

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